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“单晶电极/室温离子液体”界面双电层
电化学和 AFM 力曲线研究

Electrochemical and AFM force curve Studies of Electric
Double Layer at “Electrode/Room-Temperature Ionic
Liquid” Interface

张 笑

指导教师姓名: 毛秉伟 教授

专 业 名 称: 物 理 化 学

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Electrochemical and AFM force curve Studies of Electric Double Layer at “Electrode/Room-Temperature Ionic Liquid” Interface

A Dissertation Submitted for the Degree of Master of Philosophy

By

Xiao Zhang

Supervised by

Prof. Bing-Wei Mao

Department of Chemistry

Xiamen University

June, 2012

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摘 要

室温离子液体作为一种新型的绿色溶剂，其特有的低蒸气压、高沸点、良好的电导率和宽的电化学窗口等性质相对于传统的水溶液体系有着广阔的应用前景，但目前对“电极/离子液体”界面双电层结构的认识依旧十分模糊。相对于水溶液体系的双电层结构而言，“电极/离子液体”界面双电层结构有着截然不同的特点和性质。近年来各种研究表明，离子液体在电极表面附近会自发形成有序的阴、阳离子相间的类固态状的层状结构，但对这种层状结构研究都还停留在较为初步的阶段，关于电极电位对层状结构中阴、阳离子排布方式和结构特征影响的系统研究至今还没有报道。因此，深入探究在不同荷电状态下单晶电极表面离子液体的“层状结构”，对我们认识电极-离子液体界面双电层有着极其重要的意义。

本论文运用原位 AFM (EC-AFM) 力曲线技术和电化学测量手段，系统研究了两种烷基侧链长度的咪唑阳离子与六氟磷酸根阴离子构成的离子液体在 Au (111) 单晶电极表面附近的层状结构的数目、厚度和稳定性及其对电位（表面电荷密度）和温度的依赖性，以期获得关于离子液体中阴、阳离子组分在界面的排列方式，为建立“电极/离子液体”界面双电层的合理模型提供实验依据。主要研究内容和结果如下：

1. 通过测量体系的零电荷电位（PZC）及电荷密度与电位曲线，了解“电极/离子液体”双电层区间的电化学行为。随后，运用 EC-AFM 力曲线技术系统研究 Au(111)/[BMI][PF₆]界面形成的层状结构随电极电位变化，通过详细的力曲线统计分析，获得了 PZC 电位以正、PZC 电位和 PZC 电位以负三个电位区间内层状结构的数目、厚度和稳定性等结构信息，并建立了反映力与电位（和表面电荷）关系的 $F-E$ 曲线，讨论了三个电位区间的层状结构的特征。结果表明：在所研究范围内（-0.9 V ~ 0.5 V），Au(111)/[BMI][PF₆]界面由富含阳离子或富含阴离子的内层和电中性的外层构成，外层层状结构是固体表面附近固有的特性，最大为三层；内层层状结构是荷电表面影响的结果，且随表面荷电荷密度的增加数目可达两层，但电位对第一内层的影响远高于第二层。由此可得的重要结论是，电极-离子液体界面的双电层实际上被束缚在小于 2 nm 的很小的范围内，且界面电场

的影响急剧衰减；而电中性外层层状结构的存在说明该电极-离子液体界面不存在荷电的分散层。

2. 将研究体系拓展到 $\text{Au}(111)/[\text{OMI}][\text{PF}_6]$ ，运用 EC-AFM 力曲线方法对比研究 $\text{Au}(111)/[\text{OMI}][\text{PF}_6]$ 界面在 PZC 电位以正、PZC 电位和 PZC 电位以负三个电位区间内层状结构的数目、厚度和稳定性等结构信息，并加以详细分析。由于 OMI^+ 较 BMI^+ 具有长得多的烷基，离子在界面中的排列可能表现出阴、阳离子排布的亚层状结构。研究发现， $\text{Au}(111)/[\text{OMI}][\text{PF}_6]$ 界面同样由富含阳离子或富含阴离子的内层和电中性的外层构成。外层层状结构是固体表面附近固有的特性，最大为一层，而内层层状结构是荷电表面影响的结果，内层数目同样为一层。同时，通过对反应亚层状结构的力曲线的详细分析和讨论，初步构建了该离子液体中阴、阳离子在界面随电极电位而变的排布方式，PZC 电位以正区间，阴离子首先吸附在电极表面，随后是阳离子的烷基链，最后是阳离子的咪唑环；而在 PZC 电位以负区间，阳离子的咪唑环首先发生吸附，继而是阳离子的烷基链，最后是阴离子；在 PZC 电位附近，阴阳离子则采取相互交叉的方式自由的吸附在电极表面。

3. 在一定的温度范围内，系统研究和比较了上述二种离子液体层状结构数目、厚度、稳定性等特征受温度的影响，从而揭示双电层结构的温度依赖性。研究发现，在 15 到 40 °C 的温度范围内，温度越低，离子液体层状结构越稳定，这是因为温度越低，离子的热运动剧烈程度越小，越有利于保持层状结构的稳定性。温度对 $[\text{OMI}][\text{PF}_6]$ 离子液体层状结构的稳定性和数目的影响比 $[\text{BMI}][\text{PF}_6]$ 要缓和：温度改变 5 °C， $[\text{OMI}][\text{PF}_6]$ 在 -1.6 V 下第一层层状结构的力值变化仅为 1 到 2 nN，而 $[\text{BMI}][\text{PF}_6]$ 在 -1.0 V 第一层层状结构的力值变化为 3 到 5 nN；较低温度下， $[\text{BMI}][\text{PF}_6]$ 中的层状结构的数目有所增加，但是 $[\text{OMI}][\text{PF}_6]$ 的层状数目始终都保持在两层，随温度的变化并不敏感。这种差异可能为两种离子液体的阳离子尺寸差异导致与电极表面的作用方式和强度差异所致；同时， $[\text{OMI}][\text{PF}_6]$ 比 $[\text{BMI}][\text{PF}_6]$ 更粘稠，温度改变对离子的热运动的影响效果不如 BMI 敏感。

关键词：界面电化学；离子液体； $\text{Au}(111)$ ；双电层；层状结构；AFM 力曲线。

Abstract

Room temperature ionic liquids, as a new type of green solvents and benefited from distinct advantages such as wide electrochemical window, low vapour pressure, and good conductivity, have found wide applications in various fields. However, the investigations of electric double layer (EDL) structure at “electrode/ionic liquid” interfaces are still in its infancy. Comparing with those in aqueous solution systems, the EDLs at electrode-ionic liquid interfaces have distinct characteristics and properties. In recent years, there are researches which have shown that ionic liquids at the vicinity of the electrode surfaces spontaneously form ordered solid-like layering structure. However, the investigations of the layering behaviors, especially their potential-dependence are still very preliminary. Therefore, further studies to enrich our knowledge of electrode-ionic liquid interfaces are very important.

By utilizing in-situ AFM (EC-AFM) as well as various electrochemical methods, systematic investigations have been carried out mainly on Au(111) single-crystal surfaces in imidazolium-based ionic liquids with different lengths of alkyl side chains, which are broadly used especially in the field of electrochemistry. Through the study of the number, thickness and stability of the layering structures from potential-dependent and temperature-dependent AFM force curve measurements, we hope to reveal the multi-natured interactions between electrode surfaces and ionic liquids, thus providing experimental evidences for establishing a rational model of “electrode/ionic liquid” interface. The main results are outlined as follows:

1. The potentials of zero charge (PZC) and Q - E curves of electrode-ionic liquid interfaces are measured to understand electrochemical behavior of the ionic liquids in the double layer regions.

2. EC-AFM force measurements are employed to investigate the layering structures at Au (111)/[BMI][PF₆] interface along with the change of the electrode potential. Through detailed statistical analysis of force curves, information about the number, thickness and stability of the layering structures at potentials positive of, close to and negative of PZC are obtained. F - E curves are constructed to discuss the

features of the layering behavior in different potential regimes. It is shown that in the studied potential region ($-0.9 \sim 0.5$ V), the Au (111)/[BMI][PF₆] interface is formed with charged interior layers and neutral exterior layers. The existence of the neutral exterior layers seems to be an inherent characteristic of ionic liquids, which can reach a maximum of 3 layers, while the charged interior layers is the result of electrostatic constraint by the surface charge, which can reach a maximum of 2 layers. So important conclusions are that the EDL structure at the “electrode/ionic liquid” interface is confined to less than 2 nm, and presence of the neutral exterior layers can prove that there is no clear diffuse layer at the electrified interface.

3. Then EC-AFM force curve investigations of the layering structures are expanded to Au(111)/[OMI][PF₆] interfaces, in which the OMI⁺ has much longer alkyl than BMI⁺ and the ions at the interface are likely to show the arrangement of anion sub-layer and cation sub-layer structures. The information about the number, thickness and stability of the layering structures at potentials positive of, close to and negative of PZC are obtained. Similar to those in BMI⁺ system, it is found that Au (111)/[OMI][PF₆] interface is formed by charged interior layers and neutral exterior layers too. But there contains only one neutral exterior layer and one charged interior layer. Meanwhile, AFM force curves containing information about the sub-layer structure are obtained. Based on detailed analysis and discussions, models about the arrangement of anions and cations at the interfaces along with the change of electrode potential are proposed. At potentials positive of PZC, anions are located at the closest to the electrode surface, followed by the octane chain in the middle, and finally the imidazole ring at the far most. At negative potential of PZC, the imidazole ring of cations is located at the closest to the electrode surface, followed by the octane chain, and finally the anions at the far most. At close to PZC, cations and anions take a chessboard-type of arrangement with their equal accessibility to the electrode surface

4. Temperature influence on the layering behaviors of the above two kinds of ionic liquid systems are investigated. It is shown that within the temperature range of 15 to 40 °C, the stability of the layering structures in both BMI⁺ and OMI⁺ systems increases as temperature decrease because of the reduced thermal perturbation.

However, the temperature influence is greater for BMI⁺ than for OMI⁺ system. At -1.6 V, variation of temperature by 5 °C , the force of [OMI][PF₆] layering structure change for only 1 to 2 nN, while the force of [BMI][PF₆] layering structure change for 3 to 5 nN at -1.0 V. In addition, at low temperature, the number of the [BMI][PF₆] layering structures increase, while that of [OMI][PF₆] layer structure maintains the same. This difference may be associated with the different molecular size; At the same time, [OMI][PF₆] is more viscous than [BMI][PF₆], so that the former could be less sensitive to temperature perturbation.

Key words: Interface electrochemistry. Ionic liquids. Au (111). Electric double layer structure. Layering structure. AFM force curves.

第一章 绪论

所有的电化学电荷转移步骤，即反应粒子得到或失去电子的步骤，都是直接在“电极/溶液”界面上实现的。换言之，“电极/溶液”界面是电子交换的场所，是实现界面反应的“客观环境”，因此其性质将对界面过程产生深刻影响。由于界面中电极一侧的表面荷电性、表面化学成键、静电作用以及热扰动的影响，溶液中的分子和/或离子在“电极/溶液”界面存在一定的分布，也因此而形成了界面双电层。“电极/溶液”界面双电层一直以来都是科学家们关注和致力于研究的课题，它有着丰富而重要的研究内容，包括溶剂分子和溶质物种等在表面的吸附及取向、界面区离子过剩浓度分布、电势分布及由此引起的界面电场对电荷转移的影响等。应当指出，体系的零电荷电位（potential of zero charge, PZC）是与体系双电层性质密切相关的特征参数，也是研究双电层宏观性质的一个参照点，因此是双电层研究的重要方面。

20 世纪中期开始流行的室温离子液体作为一种新兴溶剂，由于具有低的蒸汽压、宽的电化学窗口以及适当的溶解性和电导率等优点，受到很多电化学家的青睐，逐渐地被广泛应用于电化学研究中。然而，与水溶液相比，“电极/离子液体”界面的研究尚处在初期阶段，虽然已有一些理论和实验方面的报道，但仍亟待开展有关双电层基本科学问题的研究，如：稀水溶液中 PZC 的判断依据是否还适用于离子液体体系，离子液体中高浓度的阴、阳离子在电极表面具有怎样的吸附行为，离子液体与电极间存在何种相互作用等。为了对“电极/离子液体”界面结构和性质有更全面和深入的理论和实践认识，电极体系的拓展，如从液体 Hg 电极到固体电极、从表面结构不确定的多晶电极到结构明确的单晶电极，是十分必要的。

近二十多年来发展起来的扫描隧道显微镜技术（Scanning Tunneling Microscopy, STM）具有表面结构敏感的特点，它可以在原子分辨的水平上揭示“电极/溶液”界面的微观结构，这一技术的发展极大地促进了界面双电层的研究。

近几年来，原子力显微镜技术（Atomic Force Microscopy,）也开始被人们广

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